Design of Organic Conductors Comprised of Fullerene and Lanthanum Triple-Decker Porphyrin Complexes

Mark Borysiak
Chemical and Biomolecular Engineering, The Ohio State University

NNIN iREU Site: National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, Japan
NNIN iREU Principal Investigator(s): Dr. Masayuki Takeuchi, Organic Nanomaterials Center, NIMS, Japan
NNIN iREU Mentor(s): Michael Frank, Organic Nanomaterials Center, NIMS, Japan
Contact: borysiak.1@osu.edu, takeuchi.masayuki@nims.go.jp, frank.michael@nims.go.jp

NNIN iREU Program

Abstract:

Over the past few years, the use of organic semiconductors in field effect transistors (OFETs) as an alternative to more traditional inorganic semiconductors has received increasing attention. This is a result of low cost production of OFETs due to solution processability, as well as other factors such as the incorporation of functionality by design [1]. Single crystal organic field effect transistors (SCOFETs) are of particular interest because they allow for the study of intrinsic charge transport properties of the organic semiconductor, and they also have shown relatively high mobility's compared to thin film OFETs due to the absence of grain boundaries [1]. The research that was conducted focused on the synthesis, purification, and characterization of a novel lanthanum triple-decker (LaTD; three porphyrinato complexes encompassing two lanthanum metal ions) complex for potential creation of a single crystal organic semiconductor. The LaTD will be used as an alternative to a cerium double decker (CeDD; two porphyrinato complexes encompassing a cerium metal ion) molecule in an already existing CeDD-fullerene C_{60} organic co-crystal (Figure 1). The CeDD-C_{60} co-crystal has shown impressive properties including anisotropic conducting behavior and a very high mobility (~ 10 cm^2 V^{-1} s_{-1}). The LaTD substitution in this co-crystal is hoped to improve the electronic transport properties of the crystal through increased spacing of the charge-carrying fullerene molecules. In addition, the novel LaTD molecule is an intriguing compound due to its tetraarylporphyrinato, homoleptic structure.

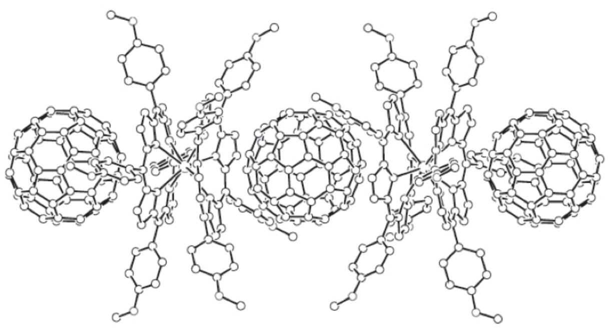

Figure 1: CeDD-C_{60} co-crystal structure.

Introduction:

There have been numerous double and triple-decker structures synthesized in the past. These structures consist of a metal ion(s) (M) sandwiched between porphyrin (P) or pthalocyanine (Pc) tetrapyrrole ligands, or a combination of the two. This results in a coordination compound in which the metal ion has a cationic charge of +3, +4, or +5 with the tetrapyrrole ligands in the -2 anionic state, forming structures of the nature $M(P)_2$, $M_2(P)_3$, or their Pc equivalents (or heteroleptic combinations) [2]. The LaTD molecule that was synthesized is of the $M_2(P)_3$ form, with the porphyrin containing four 4-methoxy phenyl substituents. The large steric compression caused by these phenyl substituents has prevented the isolation of homoleptic, tetraarylporphyrin triple-deckers in the past [2]. As a result, the LaTD molecule that was synthesized is a novel compound, most likely stabilized by the very large ionic radius of lanthanum (1.16 pm), as compared to other double or triple-decker forming metal ions.

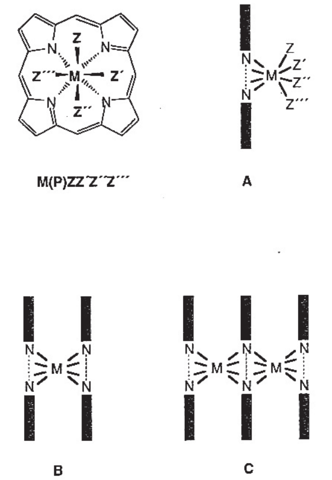

Figure 2: Triple-decker mechanism (Image Source: [2] Buchler and Ng).

The synthesis of the LaTD molecule begins by metal insertion, yielding a monoporphyrinate of octacoordinate chemistry, stabilized by ligands (Figure 2a) [2]. A raise-by-one-story reaction of this metal mono(porphyrinate) with another porphyrinate results in a double-decker structure (Figure 2b) [2]. Another raise-by-one-story reaction with the double-decker structure and a third porphyrinate results in the triple-decker structure (Figure 2c).

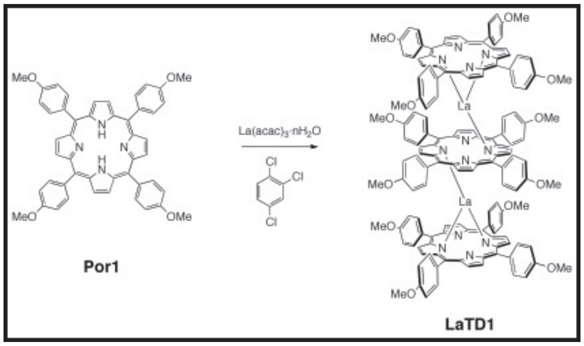

Figure 3: LaTD synthesis.

Experimental Procedure:

Synthesis of dilanthanum(III)tris[5,10,15,20-tetrakis-(4-methoxyphenyl) porphyrinate], LaTD (Figure 3). 3.74 g (8.56 mmol) of tris(acetylacetonato) lanthanum(III) n-hydrate, La(acac)$_3$n-H$_2$0, 99.9% (purchased from Wako Chemicals) and 710 mg (0.966 mmol) of 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphyrin (prepared from 4-methoxybenzaldehyde and pyrrole in propionic acid) in 96 mL of 1,2,4-trichlorobenzene (purchased from Kanto Chemical) was refluxed at 260-280°C for 36 hours under argon atmosphere. The solution started out purple and changed to a dark brown/black color as the reaction progressed. After 36 h, the TCB was removed via vacuum at a bath temperature of 100°C. The resulting solid was vacuum filtered, washed with hexane in which it is insoluble, and collected with chloroform. Using silica gel chromatography on the sample, a dark brown fraction was eluted following a purple, fluorescent fraction. The dark brown fraction was further purified via size exclusion chromatography (SEC) with chloroform. The sample was recrystallized using either methanol or ethanol, purified via recycling GPC, and re-precipitated using a toluene-hexane mixture (1:1). The final sample was taken to dryness in vacuum. The resulting LaTD solid (36.49 mg, 4.6%) was characterized using MALDI-TOF mass spectroscopy, ^{1}H NMR spectroscopy, GPC, thin layer chromatography and elemental analysis.

Results and Discussion:

The synthesis of the LaTD was confirmed through MALDI-TOF mass spectrometry (Figure 4). The molecular weight (2475 amu) is clearly shown after purification of the sample, demonstrating the clear presence of LaTD. The reaction was found to have a greater yield with increased temperature and time of reaction, although the increase in temperature is also believed to introduce bi-products that were difficult to remove. After the trial of many purification techniques, it was determined that re-precipitation using toluene and hexane was the most efficient and effective method for final purification of the sample. The sample was characterized via ^{1}H NMR spectroscopy, GPC, and elemental analysis, showing high purity, allowing the LaTD to be used in the creation of co-crystals with C$_{60}$. At the time of writing, the results of these crystals are unknown.

Conclusion and Future Work:

A novel LaTD molecule was successfully synthesized, purified, and characterized. The substitution of this molecule in place of CeDD in a CeDD-C$_{60}$ co-crystal is anticipated to improve an already impressive electron mobility of ~ 10 cm^2 V^{-1} s^{-1} for use as a single crystal organic semiconductor. Future work on this project will depend heavily on the results of the co-crystal formation, but consists of improving reaction yield, further characterization, and modifications to the LaTD/crystal structure.

Acknowledgements:

I would like to thank the National Science Foundation, National Nanotechnology Infrastructure Network Research Experience for Undergraduates program, and the National Institute Materials Science of Japan for the funding and opportunity to participate in this great program. In addition, I would like to thank my PI, Dr. Masayuki Takeuchi for the opportunity to work with his outstanding group and my mentor Mike Frank for his assistance throughout my project.

References:

[1] Reese, C. and Bao, Z. "Organic single-crystal field-effect transistors." Materials Today. March 2007.

[2] Buchler J. and Ng D. "Metal Tetrapyrrole Double and Triple-Deckers with Special Emphasis on Porphyrin Systems." Inorganic, Organometallic, and Coordination Chemistry.

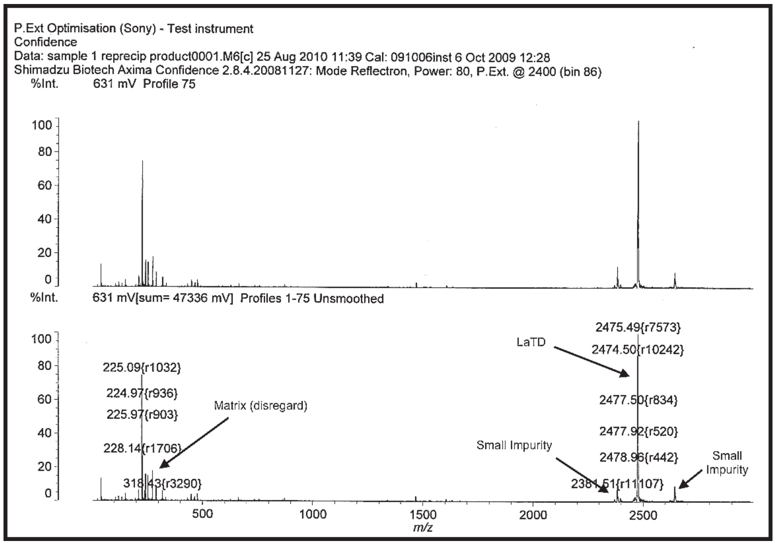

Figure 4: MALDI-TOF mass spectrum of sample (LaTD MW = 2475 amu).